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electrode layer 60 is deposited on the second insulating layer 50. The second electrode layer 60 consists of a plurality of parallel line electrodes perpendicular to the columns of electrodes in the first insulating layer 10. Display electronics (not shown) are used to modulate a voltage across the first and second electrode layers 20 and 60 to cause the phosphor layer 40 to luminesce.

A key to improved performance of the TFEL devices of the present invention was the recognition by the inventors of the contributions of the two respective insulating layers 30 and 50 to device performance. The ability of the device to fuse in the event of electrical breakdown is critical to prevent electrical breakdowns from propagating throughout the device and rendering large areas incapable of luminescence. The inventors have discovered that the first insulating layer 30 contributes almost nothing to the fusing characteristics of the display device. Instead, the fusing characteristics of a TFEL device depend primarily on the second insulating layer 50, and to a lesser extent on the phosphor layer 40. Thus, to achieve superior performance, materials may be selected for the first and second insulating layers 30 and 50 to maximize the contributions of the two layers to device performance.

Because the first insulating layer 30 contributes little to the fusing properties of the device, the material for the first insulating layer 30 may be selected to provide superior electrical strength. It has been found that electrical breakdown typically occurs at the edges 22 of the columns in the first electrode layer 20. Typically, the edges 22 of the electrodes 20 are highly nonuniform, exhibiting sharp edges and rough surfaces, and it is at these nonuniformities that electrical breakdown typically occurs. The first insulating layer 30 therefore should provide good conformal coverage of the electrode layer 20 in order to minimize the possibility of electrical breakdown. In addition, the first insulating layer 30 should have a high "figure of merit." The "figure of merit," as used herein, is the product of the dielectric constant and the electrical breakdown field of the material. A high dielectric constant improves device efficiency by increasing the capacitance of the first insulating layer. A high electrical breakdown field is also desirable, because this improves the ability of the device to be operated at higher electric potentials.

Referring to FIG. 1, in TFEL device 5, the first insulating layer 30 comprises layer 32 and optional layer 34. Layer 32 is a layer of ATO deposited using ALE. It has been found that ATO deposited by atomic layer epitaxy provides good conformal coating of the electrodes. In addition, ATO has a dielectric constant of 16 and a breakdown field of 5.5 (MV/cm), resulting in a relatively high figure of merit of 88. While ALE provides good conformal coverage of the electrodes, other chemical vapor deposition techniques should also produce good conformal coverage.

Because the second insulating layer 50 provides the greatest contribution to fusing, a material is chosen for the second insulating layer 50 which provides good fusing characteristics. Accordingly second insulating layer 50 in TFEL device 5 is a fusing dielectric material such as SiON, which exhibits good fusing characteristics. Other dielectric materials which exhibit fusing include  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ . In contrast, such materials as  $\text{TiO}_2$ , ATO and  $\text{Ta}_2\text{O}_5$  have been found not to provide fusing. Because ALE cannot be used to deposit SiON, the second insulating layer 50 is deposited using physical vapor deposition. This results in an unconventional manufacturing process in which the first insulating layer 30 and second insulating layer 50 are deposited using different deposition processes.

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Thus, the present invention combines the best features of the two different types of processes used to make TFEL devices. Surprisingly, this results in a TFEL device having superior electrical strength and fusing capabilities compared to conventional TFEL devices constructed using a single process to deposit both insulating layers. Using ATO in the first insulating layer 30 provides good conformal coating of the first electrode layer 20. In addition, the ATO has a relatively high dielectric constant as well as a relatively large breakdown field. Thus, ATO, as a first insulating layer 30 provides excellent electrical strength. In contrast, the use of SiON in the second insulating layer 50 provides good fusing characteristics. In addition, a relatively thin SiON layer can be used as the second insulating layer, avoiding a large voltage drop due to the low dielectric constant of SiON. Thus, the structure takes advantage of the relative strengths of ATO and SiON where they are needed and minimizes their weaknesses.

The TFEL device 5 is constructed using essentially the same process as is used to create conventional TFEL devices using physical vapor deposition for the insulating layers, except for the use of chemical vapor deposition (atomic layer epitaxy) to deposit the first insulating layer 30. Because the ALE process uniformly covers the entire first electrode layer 20, a contact clear must be performed by grinding away or otherwise removing a portion of the first insulating layer 30 to allow electrical contact to the first electrode layer 20. The contact clear may be performed immediately after deposition of the first insulating layer 30, or may be done after the TFEL device is annealed.

In a preferred embodiment, the second insulating layer 30 of the TFEL device 5 includes a layer 34. It has been found that an additional layer 34 of SiON improves the visual quality of the TFEL device 5 at low luminance levels. This thin layer has been found to improve phosphor nucleation uniformity and to reduce or eliminate residue artifacts from the ATO surface of the first insulating layer 30 if the ATO contact clear is done before the phosphor layer 40 is deposited.

#### EXAMPLE 1

A TFEL device 5 was constructed as follows. A first electrode layer 20 of ITO was patterned on a substrate. A first insulating layer 30 of ATO approximately 1,800 angstroms thick was deposited using atomic layer epitaxy. A 9,000 angstroms thick phosphor layer 40 of  $\text{ZnS:Mn}$  was then deposited. A second insulating layer 50 of SiON 1,100 angstroms thick was then deposited using physical vapor deposition. A second electrode layer 60 was then deposited on the second insulating layer 50.

#### EXAMPLE 2

A TFEL device 5 was constructed using the same materials and processes as in Example 1, except including additional layer 34. A layer 34 of SiON 100 angstroms thick was deposited using physical vapor deposition.

The thicknesses of the respective layers may be chosen as desired for particular applications. It has been found that TFEL device 5 can be made with the first insulating layer 30 of ATO reduced to 1,400 angstroms thick and the second insulating layer 50 of SiON reduced to about 700 angstroms for moderate phosphor thicknesses (less than 10,000 angstroms).

FIG. 2 illustrates the superior performance of the TFEL device 5 of Example 2 compared to a conventional SiON TFEL device. The TFEL device 5 displays superior

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## ALD METHOD TO IMPROVE SURFACE COVERAGE

### FIELD OF THE INVENTION

[0001] The invention relates to a method for depositing a film on a substrate in a semiconductor device, and more particularly, to an atomic layer deposition process for improving surface coverage using an adherent material. The invention also relates to novel film compositions having successive layers built upon a material which is adsorbed onto the surface of a substrate.

### BACKGROUND OF THE INVENTION

[0002] Various technologies have now been developed for applying thin films to substrates used in manufacturing semiconductor devices. Among the more established techniques is Chemical Vapor Deposition (CVD). Atomic Layer Deposition (ALD), a variant of CVD, is a relatively newer technology now emerging as a potentially superior method of achieving highly uniform, conformal film deposition. ALD, although a slower process than CVD, has often demonstrated an outstanding ability to maintain ultra-uniform thin deposition layers over complex topology. This is at least partially true because ALD is not as flux dependent as is CVD. This flux-independent nature of ALD allows processing at lower temperatures than with conventional CVD methods.

[0003] ALD processes proceed by chemisorption at the deposition surface of the substrate. The technology of ALD is based on concepts of atomic layer epitaxy developed years earlier for growing polycrystalline and amorphous films of zinc sulfide, for example, and dielectric oxides for electroluminescent display devices. The technique of ALD is based on the principle of the formation of a saturated monolayer of reactive precursor molecules by chemisorption. In ALD appropriate reactive precursors are alternately pulsed into a deposition chamber. Each injection of a reactive precursor is separated by an inert gas, e.g. Ar, purge. Each precursor injection provides a new atomic layer additive to previously deposited layers to form a uniform layer of solid film. The cycle can be repeated until the desired film thickness is attained. Thus, the introduction of the gas Ax is followed by introduction of a gas By to form a layer of AB material. This process of introducing Ax and then By can be repeated a number of times to achieve an AB film of a desired thickness.

[0004] While ALD typically allows for the formation of high quality, uniform films across a wide array of surface topologies, problems can still arise. In general, deposition initiation, i.e. formation of the first layer or few layers, is often the most problematic stage of film formation with ALD. In the preceding example, for instance, the subgroup x on the Ax gas can be a large, bulky molecule which can sterically hinder the formation of a continuous monolayer. In addition, the chemisorbent nature of Ax may be such that while it adheres adequately to the underlying substrate, it can adsorb to other materials and thereby interfere with the subsequent reaction of compounds utilized to form succeeding layers.

[0005] What is therefore needed in the art is a new method of ALD which overcomes the disadvantages associated with

this deposition technique. Also needed is a new film composition for use on a wide array of substrates in semiconductor devices.

### SUMMARY OF THE INVENTION

[0006] The invention provides a method of depositing a film on a substrate in a semiconductor device. Using ALD process conditions hereinafter described, the substrate is first exposed to at least one adherent material in a quantity sufficient for the material to adhere or adsorb onto the surface of the substrate and thereby form an initiation layer over the substrate. The initiation layer presents at least one first reactive moiety which is then chemically reacted with at least one first reaction material to form a second reactive moiety. The second reactive moiety is then chemically reacted with at least one second reaction material so as to form a reaction layer over the initiation layer. The initiation layer is not substantially degraded during formation of the reaction layer, and together with the reaction layer can constitute the final film. Additional reaction layers may also be formed over the initiation layer, and all these layers together will then constitute the final film.

[0007] In a further aspect of the invention, there is provided a film suitable for use on a substrate in a semiconductor device. The film has an initiation layer of an adherent material, and one or more reaction layers formed over the initiation layer. Each of the reaction layers may be comprised of a metal or metal-bearing compound.

[0008] Additional advantages and features of the present invention will become more readily apparent from the following detailed description and drawings which illustrate various embodiments of the invention.

### BRIEF DESCRIPTION OF THE DRAWINGS

[0009] FIG. 1 is a cross-sectional view of a semiconductor device in an intermediate stage of fabrication.

[0010] FIGS. 2A and 2B are cross-sectional views of the device shown in FIG. 1 in further stages of fabrication.

[0011] FIGS. 3A and 3B are cross sectional views of the device shown in FIG. 2 in further stages of fabrication.

[0012] FIGS. 4A, 4B, 4C and 4D are cross sectional views of the device shown in FIG. 2 in further stages of fabrication.

[0013] FIGS. 5A, 5B, 5C and 5D are cross sectional views of a semiconductor device in successive stages of fabrication according to an alternative embodiment of the invention.

[0014] FIG. 6 is a cross sectional view of a semiconductor device illustrating a barrier film according an embodiment of the invention.

[0015] FIG. 7 is a cross sectional view of a semiconductor gate stack showing a silicon dioxide film according to an embodiment of the invention.

[0016] FIG. 8 is a block diagram of a typical processor based system which includes integrated circuits that utilize the film(s) of the present invention.

### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0017] The invention relates to the formation of film on substrates in semiconductor devices using atomic layer deposition (ALD).

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vacuum pump 38 ending the first cycle. The process cycle can then repeat to form the desired thickness of the film.

[0032] If the film to be deposited is electrically conducting, reactor vessel 2 will be coated by a conducting film which eventually shields out the exciting electric field provided by the solenoidal coil 14. To avoid unnecessary reactor vessel cleaning, in another embodiment, the present invention provides the reactor vessel 3 as shown in FIG. 3. The exhaust flange 4 provides access to the interior of the reactor vessel 3. The flow of second reactant 42 is generated in a radical generator 44 which is attached to the wall of the reactor vessel 3. As before the first reactant 28 is provided from the bottle 30 and introduced to the reactor vessel 3 through the valve 20 and the manifold 18. In this embodiment, the part holder 10 can be either a metal or a ceramic. Again the microcontroller 40 controls all valves and the radical generator 44.

[0033] The radical generator 44, suitable for use with the reactor vessel 3, shown in FIG. 3, can take on many well known arrangements. One arrangement is to use a miniaturized version of the quartz tube 2 and RF coil 14 described in FIG. 1. In this arrangement, the only modification is to provide an end plate with a small hole in it, so that the radicals can flow rapidly into the reactor vessel 3 through such a nozzle. One illustration of a suitable end plate with a hole in it serving as a nozzle is shown in FIG. 1, as a stainless steel anode, in a paper by A. Sherman, *In situ Removal of Native Oxide from Silicon Wafers*, J. Vac. Sci. Technol. Vol. B8(4), 656 (Jul/Aug 1990) which paper is incorporated by reference here in its entirety. This paper also describes generating hydrogen radicals using a hollow cathode DC discharge chamber. Other alternatives are reviewed for hydrogen radical generation in a recent paper by V. M. Bermudez, *Simple, Efficient Technique for Exposing Surfaces to Hydrogen Atoms*, J. Vac. Sci. Technol. Vol. A14, 2671 (1996). Similar techniques can be also used to generate any of the radicals that might be needed to form the elemental films described herein.

[0034] Concerns about the uniformity of distribution of radicals should not control the type of radical generator 44 to be employed. As long as sufficient radicals are generated to react the first reactant, any excess radicals play no role in the film formation. More important considerations relate to avoiding the introduction of contaminants, the cost of the radical generator, and simplicity of its operation. Also, the reaction between any one of the first reactants adsorbed on the part surface and the radical flux to the part, should be rapid and independent of surface temperature. Therefore, it should be possible to carry out these thin film depositions at lower temperatures than in conventional sequential chemical vapor deposition processes which are typically carried out at 300-600° C.

[0035] One of the difficulties in the commercial application of traditional sequential chemical vapor deposition processes, is that they deposit films slowly. For very thin films (e.g. 100 Å) this is of little concern. However, if thicker films are required (e.g., 1 μm or 10,000 Å), then the commercial viability of some applications may be in question.

[0036] In the present process, by virtue of the use of remotely generated, very reactive, radicals (e.g. oxygen atoms, hydrogen atoms, nitrogen atoms, etc.) we are able to

operate the process at room temperature. This fact gives rise to two features of this process that can lead to higher throughput from the reactor used.

[0037] When the first reactant is exposed to the substrate at room temperature, it is possible for more than one monolayer to remain behind after the reactor is evacuated with a vacuum pump. In fact, if the substrate temperature is lowered enough we would find the precursor condensing to a liquid film on the substrate surface—obviously not the way to operate the present process. Then when the substrate, with multiple monolayers remaining on its surface, is exposed to the second reactant (radical) more than one monolayer of product film can be grown in each cycle. Our experimental data has verified that 3 Å of Al<sub>2</sub>O<sub>3</sub> grows per cycle from TMA and oxygen atoms at room temperature. All other studies of Al<sub>2</sub>O<sub>3</sub> formed in thermal (e.g. high temperature) sequential CVD shows deposition rates of less than 1 Å/cycle.

[0038] Second, if we do not have to fully evacuate the reactor chamber after each precursor exposure in our process, we could shorten the time for each cycle. In the flow type reactor described by Suntola in U.S. Pat. No. 4,389,973, he used an inert gas to purge each reactant after each exposure of the substrate. Typically nitrogen gas was used as the purge gas. In our case, the second reactant is created by striking a glow discharge in an otherwise inert gas (e.g. O<sub>2</sub>→O). Therefore, there is no need to use a separate inert gas to purge the first reactant. We can simply use the second gas with the discharge turned off. Again, it is not necessary to purge the second reactant, because it goes away when we extinguish the glow discharge. By eliminating the separate purge gas, we can shorten and simplify the deposition cycle. This will enable a shortening of the cycle time.

[0039] It should be recognized, however, that there are some instances where using a purge gas to separate the two reactants in a sequential CVD reactor may not be the most desirable way to operate the system. When substrates are being coated that have features with high aspect ratio holes or trenches it will, in general, be more effective to use the vacuum pump out style described earlier. This will be the case, because it would be harder for a given reactant to diffuse through an inert gas down to the bottom of a hole when the hole is filled with inert gas. For those applications where high aspect ratio holes do not have to be coated (e.g., large area flat panel displays), then the inert gas purge would be suitable. In that case, using the gas in which a glow discharge is created as the inert gas (with glow discharge off) for a purge operation should enhance throughput.

[0040] Finally, when very thin films of dielectric materials (e.g., Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>) are deposited by a sequential CVD process, the surface may have a substantial degree of roughness in spite of the layer by layer method of deposition. Apparently, this phenomenon is caused by some poorly understood agglomeration process as the film is growing. One technique that can be used to avoid this surface roughening would be to grow many thin layers where two similar materials alternate. For example, if we want a 100 Å film we could grow, alternately, 10 Å layers of Al<sub>2</sub>O<sub>3</sub> and 10 Å layers of Si<sub>3</sub>N<sub>4</sub> and do it 5 times. This should produce a dielectric layer with a dielectric constant of about 7-8, which is a good diffusion barrier and has good electrical breakdown strength, and which is also very flat. By using the new method

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## SEQUENTIAL CHEMICAL VAPOR DEPOSITION

## BACKGROUND OF THE INVENTION

[0001] This application is a continuation-in-part of U.S. Application No. 081699,002, filed on Aug. 16, 1996, which is incorporated herein by reference. The present invention relates to methods and apparatuses suited to the low temperature deposition of solid thin films of one or more elements by the technique of sequentially exposing the object being coated with chemically reactive gaseous species. It also describes a number of applications of films produced by such processes.

[0002] CVD Reactor Technology

[0003] Chemical vapor deposition (CVD) reactors have been used for decades to deposit solid thin films and typical applications are coating tools, manufacture of integrated circuits, and coating jewelry. A. Sherman, *Chemical Vapor Deposition for Microelectronics*, Noyes Publications, New Jersey, 1987. Up to the 1960's many CVD reactors operated by exposing a heated object or substrate to the steady flow of a chemically reactive gas or gases at either atmospheric or reduced pressures. Since, in general, it has been desired to deposit films at as high a rate as possible as well as at as low a temperature as practical, the gases used to produce the film are extremely reactive (e.g., silane plus oxygen to deposit silicon dioxide). Then if the gases are allowed to mix for too long a time period before impinging the substrate, gas phase reactions can occur, and in extreme cases there can be gas phase nucleation and particles formed rather than deposition of continuous films. At the same time, the high rate of deposition and the reactive gases used makes it very difficult to coat large area substrates uniformly. This results in very complex and expensive commercial CVD reactors. A further complication with this method is that in some cases the films deposited do not conformally coat non-uniform surfaces. This can be particularly deleterious in the manufacture of integrated circuits.

[0004] In the 1960's it was realized that we could lower the temperature required for thin film deposition at acceptable rates by creating a low pressure glow discharge in the reactive gas mixture. The glow discharge produces many high energy electrons that partially decompose the reactive gases, and these gas fragments (radicals) are very reactive when they impinge on a surface even at moderate temperatures. Although using a glow discharge allows lower temperature operation, commercial reactors are very complex and expensive, since uniform deposition over large area substrates is even more difficult due to the inherent nonuniformity of glow discharges and due to the added expense of complex high frequency power supplies. Also, this technique can often lead to degradation of the film conformality, due to the highly reactive nature of the radicals.

[0005] In the 1970's atomic layer epitaxy (ALE) was developed in Finland by T. Suntola and J. Anston. U.S. Pat. No. 4,058,430 describes how they grew solid thin films on heated objects. This process involves exposing the heated surface to a first evaporated gaseous element, allowing a monolayer of the element to form on the surface, and then removing the excess by evacuating the chamber with a vacuum pump. When a layer of atoms or molecules one atom or molecule thick cover all or part of a surface; it is referred to as a monolayer. Next, a second evaporated

gaseous element is introduced into the reactor chamber. The first and second elements combine to produce a solid thin compound monolayer film. Once the compound film has been formed, the excess of the second element is removed by again evacuating the chamber with the vacuum pump. The desired film thickness is built up by repeating the process cycle many (e.g., thousands) times.

[0006] An improvement to this technique was described in a later patent issuing in 1983 to T. Suntola, A. Paakala and S. Lindfors, U.S. Pat. No. 4,389,973. Their films were grown from gaseous compounds rather than evaporated elements so the process more closely resembles CVD. This was recognized to be especially advantageous when one component of the desired film is a metal with low vapor pressure, since evaporation of metals is a difficult process to control. With this approach, films were deposited by flow reactors similar to a conventional CVD reactor, where the excess of each gas is removed by flowing a purge gas through the reactor between each exposure cycle. This approach was limited to only a few films, depending on the available gaseous precursors, and all of these films were not as contamination free as desired. We will refer to this process as sequential chemical vapor deposition.

[0007] An alternative approach to operating a sequential chemical vapor deposition reactor would be to operate a non-flow vacuum system where the excess gaseous compound of each sequence is removed by vacuum pumps in a manner similar to the original Suntola 1977 process. H. Kumagai, K. Toyoda, M. Matsumoto and M. Obara, *Comparative Study of  $Al_2O_3$  Optical Crystalline Thin Films Grown by Vapor Combinations of  $Al(CH_3)_3/N_2O$  and  $Al(CH_3)_3/H_2O_2$* , Jpn. Appl. Phys. Vol. 32, 6137 (1993).

[0008] An early application of sequential chemical vapor deposition was for deposition of polycrystalline ZnS thin films for use in electrochromic flat panel displays. M. Leskela, *Atomic Layer Epitaxy in the Growth of Polycrystalline and Amorphous Films*, Acta Polytechnica Scandinavica, Chapter 195, 1990. Additional studies have shown that other commercially important solid films of different compounds, amorphous and polycrystalline, can be deposited by this technique on large area glass substrates. Among these other films are sulfides (strontium sulfide, calcium sulfide), transition metal nitrides (titanium nitride) and oxides (indium tin oxide, titanium dioxide). Elsewhere, this technique has been developed as a means of depositing epitaxial layers of group III-V (gallium indium phosphide) and group II-VI (zinc selenide) semiconductors, as an alternative to the much more expensive molecular beam epitaxy process.

[0009] To applicant's knowledge the only literature discussing sequential chemical vapor deposition of elemental films are those that deposit elemental semiconductors in group IVB such as silicon and germanium. One such study, S. M. Bedair, *Atomic Layer Epitaxy Deposition Process*, J. Vac. Sci. Technol. B 12(1), 179 (1994) describes the deposition of silicon from dichlorosilane and atomic hydrogen produced by a hot tungsten filament. By operating the process at 650° C. deposition of epitaxial films are described. Deposition of diamond, tin and lead films, in addition to silicon and germanium by an extraction/exchange method in conjunction with a sequential processing scheme similar to sequential chemical vapor deposition has also been reported M. Yoder, U.S. Pat. No. 5,225,366. Also

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